

Hückel Theory

CHEMISTRY 2310: ADVANCED ORGANIC CHEMISTRY 1

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The variational method and linear combination of atomic orbitals (LCAOs)

Suppose we wanted to solve the eigenvalue problem $\hat{H}\psi = E\psi$ for an n -atom system, but we have no idea what the mathematical expression for wavefunction ψ looks like. The variational method is a tool that nevertheless allows us to gain insight into its properties. First, recall that if ψ is a normalized solution to the eigenvalue problem, the expectation value of energy is given by

$$E = E \int \psi^* \psi = \int \psi^* (E\psi) = \int \psi^* \hat{H} \psi.$$

(All integrals in this handout are over all space \mathbb{R}^3 , with respect to volume element $d\tau = dx dy dz$.) The variational theorem allows us to make and optimize a guess.

Let E_0 be the smallest eigenvalue (i.e., ground state energy) with corresponding wavefunction ψ_0 , and suppose ψ_g is a guessed (fancy word: *ansatz*) wavefunction. If we define the functional¹ $\mathcal{E} : \varphi \mapsto \int \varphi^* \hat{H} \varphi$, then the **variational theorem** states that

$$\mathcal{E}[\psi_g] \geq E_0,$$

with equality holding if and only if $\psi_g = \psi_0$. In other words, if ψ_g has optimizable parameters c_1, \dots, c_n , minimizing $\mathcal{E}[\psi_g(c_1, \dots, c_n)]$ with respect to these parameters will get us closer to the true ground state energy (and wavefunction) without having to worry about “overshooting.”

If we have a set of normalized atomic orbitals (AOs) ϕ_1, \dots, ϕ_n for our system, we have a good place to start optimizing: let $\psi_g = N(c_1\phi_1 + \dots + c_n\phi_n)$, where N is a normalization constant. Thus, our molecular orbitals (MOs) will be formed as **linear combinations of atomic orbitals** (LCAOs). (Molecular orbitals are not really LCAOs but this assumption is a convenient approximation.) Moreover, we will assume these wavefunctions are all real, so that $\phi_i = \phi_i^*$. As our first order of business, we want to normalize ψ_g by determining what N should be, so we set

$$\int \psi_g^2 = N^2 \int (c_1\phi_1 + \dots + c_n\phi_n)^2 = N^2 [c_1^2 \int \phi_1^2 + \dots + c_n^2 \int \phi_n^2 + 2 \sum_{i < j} c_i c_j \int \phi_i \phi_j] = 1.$$

We can simplify this by defining $S_{ij} := \int \phi_i \phi_j$ (called the overlap integral for $i \neq j$; $S_{ii} = 1$ is simply the normalization condition for each ϕ_i), so we obtain the value of N :

$$N = \left[\sum_i c_i^2 S_{ii} + 2 \sum_{i < j} c_i c_j S_{ij} \right]^{-1/2}.$$

The task at hand is to minimize $\mathcal{E}[\psi_g] = \int \psi_g \hat{H} \psi_g$:

$$\begin{aligned} \int \psi_g \hat{H} \psi_g &= N^2 \int (c_1\phi_1 + \dots + c_n\phi_n) \hat{H} (c_1\phi_1 + \dots + c_n\phi_n) \\ &= N^2 [c_1^2 \int \phi_1 \hat{H} \phi_1 + \dots + c_n^2 \int \phi_n \hat{H} \phi_n + 2 \sum_{i < j} c_i c_j \int \phi_i \hat{H} \phi_j] \\ &= N^2 \left[\sum_i c_i^2 H_{ii} + 2 \sum_{i < j} c_i c_j H_{ij} \right], \quad (*) \end{aligned}$$

where we used the abbreviation $H_{ij} := \int \phi_i \hat{H} \phi_j$ (called the Coulomb integral when $i = j$ and exchange integral when $i \neq j$), and the fact (Hermitian property of the Hamiltonian) that $\int \phi_i \hat{H} \phi_j = \int \phi_j \hat{H} \phi_i$.

When \mathcal{E} reaches its minimum value, the partial derivatives of \mathcal{E} with respect to the coefficients c_i are all zero: $\partial \mathcal{E} / \partial c_i = 0$ ($i = 1, \dots, n$).

¹A functional is a type of function that takes a function as its input and outputs a (real) number.

Rewriting (*) as $\mathcal{E} \cdot [\sum_i c_i^2 S_{ii} + 2 \sum_{i < j} c_i c_j S_{ij}] = \sum_i c_i^2 H_{ii} + 2 \sum_{i < j} c_i c_j H_{ij}$ and differentiating both sides of the equality with respect to c_i , we obtain (after combining terms) $\mathcal{E} \cdot (\sum_j 2 c_j S_{ij}) = \sum_j 2 c_j H_{ij}$, or $\sum_j c_j (H_{ij} - \mathcal{E} S_{ij}) = 0$ ($i = 1, 2, \dots, n$).

Using matrices, we can combine these n equations as

$$\begin{bmatrix} H_{11} - \mathcal{E} S_{11} & H_{12} - \mathcal{E} S_{12} & \cdots & H_{1n} - \mathcal{E} S_{1n} \\ H_{21} - \mathcal{E} S_{21} & H_{22} - \mathcal{E} S_{22} & \cdots & H_{2n} - \mathcal{E} S_{2n} \\ \vdots & \vdots & & \vdots \\ H_{n1} - \mathcal{E} S_{n1} & H_{n2} - \mathcal{E} S_{n2} & \cdots & H_{nn} - \mathcal{E} S_{nn} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix}.$$

By a theorem of linear algebra, this homogeneous matrix equation has nontrivial solutions (a solution other than $c_1 = \dots = c_n = 0$) if and only if the $n \times n$ matrix is singular:

$$\det([H_{ij} - \mathcal{E} S_{ij}]_{n \times n}) = 0 \quad (\text{the secular determinant}).$$

Physical interpretation and the Hückel assumptions

The integrals H_{ii} , H_{ij} , S_{ij} admit relatively concrete physical interpretations. The **Coulomb integral** H_{ii} is the energy of an electron in AO ϕ_i before interaction, while the **exchange integral** (also called the **resonance integral**) H_{ij} ($i \neq j$) is the energy of stabilization by allowing an electron to delocalize between ϕ_i and ϕ_j (or, roughly, the strength of the interaction between the orbitals). The **overlap integral** S_{ij} ($i \neq j$) expresses the extent of spatial overlap between the electron densities of ϕ_i and ϕ_j .

Hückel MO theory is a greatly simplified theory that deals with the π -electrons only of a molecule and assumes that the σ -electrons form the molecular framework but can otherwise be ignored. In the simplest version of Hückel theory dealing with unsaturated hydrocarbons, all H_{ii} are equal and set to the energy of a carbon 2p orbital and is designated by α : $H_{ii} = \alpha$.

Simplifying assumption 1: Only p orbitals on carbons i, j that are σ -bonded to each other are considered to interact with energy β : $H_{ij} = \beta$ (i, j neighbors). For non-neighboring and non-identical i, j , $H_{ij} = 0$. The signs of α and β are negative by convention.

Simplifying assumption 2: All overlap integrals are set to zero: $S_{ij} = 0$ ($i \neq j$), while because the AO's are already assumed to be normalized, we can write $S_{ii} = \int \phi_i \phi_i = 1$.

Neglecting overlap is a drastic assumption! Moreover, there is an important consequence of having nonzero (positive) overlap integrals: *Bonding orbitals are less stabilized than antibonding orbitals are destabilized*: If bonding and antibonding orbitals are both filled, the overall interaction is destabilizing! However, we do not see this in the Hückel approximation because overlap is set to zero.

EXAMPLE: Consider the allyl system, with atoms numbered from left to right as 1, 2, and 3. Using the standard Hückel theory variable names, the secular determinant is

$$\begin{vmatrix} \alpha - \mathcal{E} & \beta & 0 \\ \beta & \alpha - \mathcal{E} & \beta \\ 0 & \beta & \alpha - \mathcal{E} \end{vmatrix} = 0.$$

To simplify notation, set $x := (\alpha - \mathcal{E})/\beta$. Then equivalently, $\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$. Using minor expansion to

evaluate the determinant, we get $x^3 - 2x = 0$, which has roots $x_1 = -\sqrt{2}$, $x_2 = 0$, and $x_3 = \sqrt{2}$, which gives orbital energies $\mathcal{E}_1 = \alpha + \sqrt{2}\beta$, $\mathcal{E}_2 = \alpha$, $\mathcal{E}_3 = \alpha - \sqrt{2}\beta$.

To work out the orbital coefficients, we plug back into the equation $\begin{bmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{bmatrix} \cdot \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$.

\mathcal{E}_1 : $(c_1, c_2, c_3) = (c_1, \sqrt{2}c_1, c_1)$, so $N = (c_1^2 + 2c_1^2 + c_1^2)^{-1/2} = \frac{1}{2c_1}$, and $\psi_1 = \frac{1}{2}\phi_1 + \frac{\sqrt{2}}{2}\phi_2 + \frac{1}{2}\phi_3$.

\mathcal{E}_2 : $(c_1, c_2, c_3) = (c_1, 0, -c_1)$, so $N = (c_1^2 + 0^2 + (-c_1)^2)^{-1/2} = \frac{1}{\sqrt{2}c_1}$, and $\psi_2 = \frac{\sqrt{2}}{2}\phi_1 - \frac{\sqrt{2}}{2}\phi_3$.

\mathcal{E}_3 : $(c_1, c_2, c_3) = (c_1, -\sqrt{2}c_1, c_1)$, so $N = (c_1^2 + 2c_1^2 + c_1^2)^{-1/2} = \frac{1}{2c_1}$, and $\psi_3 = \frac{1}{2}\phi_1 - \frac{\sqrt{2}}{2}\phi_2 + \frac{1}{2}\phi_3$.

Note that normalization by $N = [\sum_i c_i^2]^{-1/2}$ is equivalent to adding the condition $\sum_i c_i^2 = 1$. ■